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(54) Title: ALKALI-RESISTANT GLASS FIBERS

(57) Abstract

Alkali-resistant glass fibers comprising about 30 to 60 percent SiO_2, 15 to 20 percent Al_2O_3, 20 to 30 percent CaO, and 1 to 10 percent Fe_2O_3. The fibers may be prepared from inexpensive materials such as slate and limestone.

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ALKALI-RESISTANT GLASS FIBERS

This invention relates to novel alkali-resistant glass fibers, and their preparation. The fibers find particular use in strengthening cement and concrete products, and may find extensive use as substitutes for asbestos in such products.

Asbestos fibers have long been used to strengthen cement and concrete products. However, since the recognition of the toxicity of asbestos there have been many attempts to develop fibers to replace it. One of the most important properties of fibers for use in cement and concrete products is resistance to chemical attack by the alkali in the cement mixtures. Because the diameter of the fibers is usually very small, e.g., about 2 to 20 micrometers, a relatively small degree of attack can cause a large decrease in mechanical strength.

The most promising substitute for asbestos to date has been zirconia-containing glass fibers. Although these fibers are fairly resistive to alkali attack, they are expensive and difficult to fabricate because of the very high melting temperatures required. Accordingly, there is a need for a fiber that is resistant to alkali attack, as well as being relatively easy and cheap to fabricate.

It has now been found, according to the present invention, that a new family of zirconia-free glass fibers, having the compositions set forth below, are highly resistant to alkali attack. In addition, these fibers are readily prepared from raw materials that are inexpensive and readily available. The fibers of the invention have the following approximate compositions, in percent by weight:

SiO_2	30-60%
Al_2O_3	15-20%
CaO	20-30%
Fe_2O_3	1-10%

It has also been found that about 1 to 7% of MgO, 2 to 8% of K_2O or 1 to 5% of Na_2O can be included in the above compositions without adversely affecting the alkali resistance of the fibers. The fibers are prepared by means of procedures conventionally employed in preparation of glass fibers, i.e., melting of the appropriate admixture of raw materials, followed by drawing or spinning to form the fibers.

The above compositions can be readily, and inexpensively, formed from mixtures of naturally occurring slate and limestone. Suitable raw materials are not, however, limited to freshly mined slate and limestone, but may include waste slate and waste marble, e.g., materials left over from mechanical working of slate and marble. In addition, other materials such as basalt may be used. The raw materials are initally ground, or otherwise reduced, to a suitable particle size, e.g., about 50 to 200 mesh, and are then admixed and melted in suitable refractory vessels such as pots or crucibles of refractory materials such as chromite, alumina, platinum, etc. Suitable melt temperatures are obtained by conventional means, such as electric furnaces or gas furnaces, and will generally range from about 1300 to 1400°C, with the optimum depending on various factors such as the specific composition of the melt, raw materials employed, and desired properties of the product fibers. The admixture is desirably maintained

at the melt temperature for a period of about 3 to 5 hours to ensure complete fusion of the ingredients.

The molten mixture is then cooled to a temperature, generally about 1100 to 1250°C, suitable for working, and fibers are formed by conventional means such as drawing at high speed through a fine orifice, or by spinning to form a glass wool. Conventional means, such as contacting with screens of appropriate mesh size, are also employed to reduce the fibers to suitable lengths. Optimum diameters and lengths of the fibers will vary with the specific use; however, diameters of about 8 to 12 microns and lengths of about 1/8 to 1/2 inch are generally most suitable for use in cement and concrete products. Fibers thus prepared have been found to have tensil strengths of about 80,000 to 150,000 psi and densities of about 2.75 to 2.95 gm/cc. Alkali resistance of the fibers has been found to be much superior to Pyrex glass and as good as commercially available alkali-resistant glasses.

The invention will be more specifically illustrated by the following example.

Example

Glass fibers were prepared from three mixtures of Vermont slate and limestone, and were compared with fibers of a commercially available alkali-resistant (AR) glass and pyrex glass. The mixtures of slate and limestone consisted, respectively, of 40% slate and 60% limestone, 50% each of slate and limestone, and 60% slate and 40% limestone. Chemical compositions, in weight %, of the slate-limestone mixtures, as well as the AR and pyrex glasses, are given in Table 1.

Table I

Slate-limestone glass

Composition	40/60	50/50	60/40	AR glass	Pyrex
SiO_2		38.6		61.0	80.9
ZrO_2				21.0	
B_2O_3					12.7
Al_2O_3		17.6		1.5	2.3
Fe_2O_3		4.72			0.03
CaO		28.0		3.0	
MgO		2.65			
Na_2O		2.16		16.5	4.0
K_2O		2.76			0.04

* Central Glass Co., U.S. Patent No. 4,066,465

The slate and limestone were ground to a particle size of 100 mesh and thoroughly mixed by means of a ball-mill. The mixtures were then melted at 1350°C in air, and were maintained at this temperature for a period of about 3-5 hrs. The melt was then cooled to 1150°C, and fibers of a diameter of 20 microns were formed by drawing. The fibers were reduced to lengths of 1/2 to 1 inch by means of mechanical cutters. These fibers, and similar fibers of AR and pyrex glasses, were then tested for

alkali resistance by reaction in 5% NaOH solution at 90°C for 4 hours. Results of the tests, as well as properties of the glasses are shown in Table 2. It is evident from the data of the table that the glasses of the invention are much superior to Pyrex and are as good as commercially available AR glasses.

Table 2

Slate-limestone glass

Properties	40/60	50/50	60/40	AR glass	Pyrex
Density (g/cm^3)	2.76	2.82	2.92	-	2.23
Melting Temp. (°C)	1300	1350	1400	1500	1400
Fiber Drawing Temp. (°C)	1150	1200	1250	1350	-
Alkali Resistance,	0.80	0.36	0.13	0.37	6.47

we claim:

1. Alkali-resistant glass fibers comprising, in percent by weight, about 30 to 60 percent SiO_2, about 15 to 20 percent Al_2O_3, about 20 to 30 percent CaO, and about 1 to 10 percent Fe_2O_3.

2. Fibers of claim 1 also containing about 1 to 7 percent MgO, about 2 to 8 percent K_2O, and/or about 1 to 5 percent Na_2O.

3. A method for preparation of the glass fibers of claims 1 or 2 comprising admixing slate and limestone, melting the admixture at a temperature of about 1300 to 1400°C, lowering the melt temperature to about 1100 to 1250°C, and forming fibers therefrom.

4. A method for strengthening cement and concrete products by incorporating therein, prior to the curing of said cement and concrete products, alkali-resistant glass fibers of the compostion of claim 1.

5. A method for strengthening cement and concrete products by incorporatiing therein, prior to the curing of said cement and concrete products, alkali-resistant glass fibers of the composition of

claim 2.

6. Alkali-resistant glass fiber reinforced cement and concrete products comprising a cementitious matrix and reinforcing alkali-resistant glass fibers having the composition of claim 1.

7. Alkali-resistant glass fiber reinforced cement and concrete products comprising a cementitious matrix and reinforcing alkali-resistant glass fibers having the composition of claim 2.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US82/01670

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[3] C04B 7/02
US 428/364, 703; 106/99

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	106/99 428/364, 703

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	US, A, 3,887,386 Published 03 June 1975, National Research and Development Corporation	1-6
Y	US, A, 4,002,482 Published 11 January 1977, JENAer Glaswerk Schott & Gen.	1-6
Y	US, A, 4,095,986 Published 20 June 1978, Director-General, agency of Industrial Science and Technology	1-6
Y	US, A, 4,153,439 Published 08 May 1979, Rockwool Aktiebolaget	1-6
X	US, A, 4,205,992 Published 03 June 1980, See column 1, lines 33-51 and column 2, line 38 et seq., Rockwool Aktiebolaget	1-6

* Special categories of cited documents: [15]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
02 February 1983	15 FEB 1983
International Searching Authority [1]	**Signature of Authorized Officer [20]**
US	W. J. VanBalen